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16. ABSTRACT

Much of the present information on the products formed when seawater is chlorinated is based on observations of laboratory experiments in which chlorine was added to seawater to stimulate conditions of electricity generating plants. Results are reported for a field study at the Port Everglades power plant of the Florida Power and Light Company to investigate reaction products from the chlorination of seawater. Observations indicate that reaction products may be quantitatively as important as the more extensively studied haloforms, with unknown environmental significance.

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CHAPTER 34

REACTION PRODUCTS FROM THE CHLORINATION OF SEAWATER

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INTRODUCTION

Much of the present information on the products formed when seawater is chlorinated is based on observations of laboratory experiments in which chlorine was added to seawater to simulate conditions of electricity generating plants. The work of Helz et al.[1] is the only comparison of laboratory simulation and direct sampling at an operating power plant that we have found in the literature. They found that chlorine-produced oxidants disappeared to a much greater extent (factor of ten) in the water that passed through the Chalk Point plant than did an equal oxidant dose under laboratory conditions or in samples withdrawn from the plumbing upstream of the condensers inside the power plant. Also, they measured only traces of haloforms in the discharge canal waters, even though 10-100 μg/l $CHBr_3$ was formed in chlorinated intake water. On some of their sampling dates, ammonia nitrogen was found to be higher in the discharge canal than in the surface water at the intake, but this feature was not observed under laboratory conditions. These discrepancies led Helz et al. to the view that "laboratory dosing of water from the intake canal with 1-2 mg/l Cl as NaOCl provided poor models for what was observed in the field."

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CHLORINATION AT THE PORT EVERGLADES PLANT

Sampling at the Port Everglades power plant of the Florida Power and Light Company was undertaken for comparison with the observations at the Chalk Point plant by Helz et al. The Port Everglades power plant consists of four oil-fired units with four condensers per unit. Cooling water is pumped from the harbor and, during our observations, had salinities of 29.5-31.3 parts per thousand (ppt), in contrast to the average salinity at the Chalk Point plant of 5 ppt. Microorganism fouling of the condensers is not a substantial problem at Port Everglades, and chlorination for 15 min/day on each condenser sequentially at a dose of 0.6 ppm is used. Samples were collected from the pipe just downstream of the circulating water pump (chlorine is injected through a manifold in the intake structure and mixing takes place in the pump) and from the discharge sluiceway. Mixing of chlorinated and unchlorinated water takes place in the discharge sluiceway and the resulting nonuniformity produces variability in replicate samples. Additional samples at the circulating pump were held in glass flasks for 2.5 min and then stabilized for comparison with the water collected at the discharge that passes through the plant in approximately 2.5 min.

Methods

The samples for residual oxidant determinations were stabilized immediately after collection by adding phenylarsine oxide (PAO) solution, and the unreacted PAO was titrated with standard iodine solution using photometric endpoint detection[2] within 24 hr of collection. Bromoform concentrations were estimated using a purge-and-trap procedure[3] with a Hewlett-Packard 5730A chromatograph and electron-capture detector (ECD). The samples for the ammonia nitrogen determinations were stabilized at collection by adding phenol solution and analyzed using the Solórzano procedure.[4]

Results

Comparison of the concentrations of residual oxidants in the discharged water and in water from the circulating water intake pump held for 2.5 min did not show a remarkable difference in the rate of disappearance of the residual oxidants. The decrease in residual oxidant concentration in either case was typically 50%.

Bromoform was found in the discharge water samples at an average concentration of 40 ppb. Intake water samples had higher concentrations that averaged 65 ppb, and the difference may be accounted for by the dilution in the discharge sluiceway.

Ammonia nitrogen in the intake water samples averaged 25 μg/l. Similar values were observed in the discharged waters and in the intake samples that were held for 2.5 min before addition of the phenol solution.

Our observations show no major effects associated with passage of the cooling water through the Port Everglades plant. Comparison with the results of Helz et al. for the Chalk Point plant suggests there must be some site-specific considerations that have not been identified. The total organic carbon (TOC) at both sites was approximately 5 mg/l and the ammonia nitrogen levels were comparable; thus, gross water quality was not strikingly different. The condensers at Chalk Point have copper-nickel tubing and those at Port Everglades have aluminum-brass tubing, but there is no information on the reactivity of chlorinated water with these materials. Observations at several coastal plants are needed for assessment of the haloform discharge rates and usefulness of laboratory chlorination studies for anticipating the nature of power plant discharges.

LOW POLARITY COMPOUNDS IN CHLORINATED SEAWATER

Compounds of low polarity (lipophilic) are of interest because of their potential for bioaccumulation with associated ecological and human health effects. To our knowledge, no work has been done on isolation and identification of such compounds in chlorinated seawater, except for the highly volatile, low-molecular-weight halocarbons. Although our work in this area is incomplete, the following information draws attention to these compounds and describes results to date.

The primary experiments consisted of chlorinating Biscayne Bay water, extraction of the reaction mixture with organic solvents [$CHCl_3$, $C_2F_3Cl_3$ or $(C_2H_5)_2O$], evaporation of the extract to produce a concentrate, and gas chromatographic/mass spectral observations on aliquots of the concentrates. The Bay water samples are estimated to be relatively rich in organic matter (5-10 mg/l carbon). The products of chlorination were found to depend on the amount of chlorine added, with bromoform, the major product, at doses of ≤ 1 ppm. With higher doses, the bromoform formation remained nearly constant (300-400 ppb) but several new peaks appeared in the chromatograms.

As an example, the observations with 11=ppm chlorine added are shown in Figure 1. Attention has been given primarily to peaks 7 and 9. These peaks produce very simple mass spectra, as shown in Figure 2. The 149-151 m/e pair strongly suggests the presence of bromine with nearly equal abundance of the 79 and 81 atomic mass isotopes. The strong signal of mass number 69 may be accounted for by the loss of HBr from the parent molecule. The 149-151 pair appears to be molecular ions, based on the persistence of these signals as the electron beam source energy is reduced and because of the formation of the same ions with methane chemical ionization. The compounds may be represented as C_4H_8NBr and sufficient material for elemental analysis is now being collected with preparative-scale gas chromatograph.

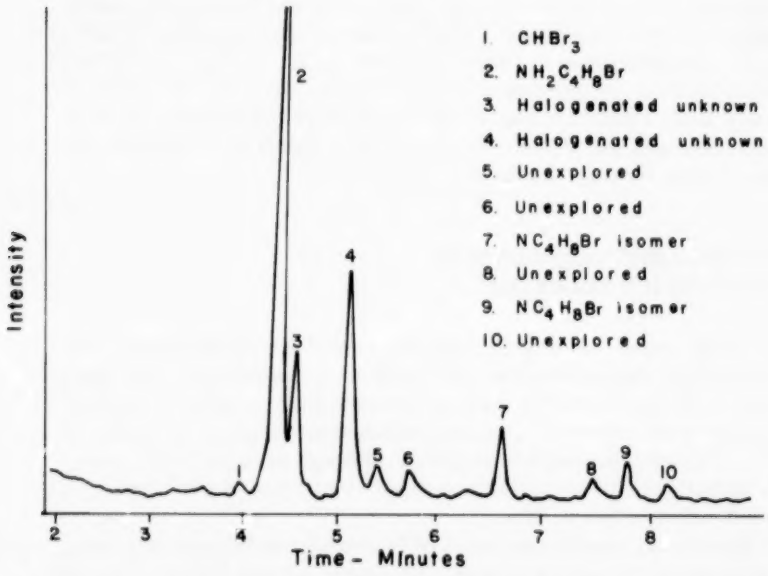

Figure 1. Total ion chromatogram of an ether extract of Biscayne Bay water chlorinated with 11 ppm Cl_2.

One possible interpretation of mass spectra obtained to date is that Peak numbers 2, 7, and 9 are nitrogen compounds containing a single bromine, i.e., $NH_2C_4H_8Br$ and NC_4H_8Br. This is contingent upon the assumption of the molecular ion having a mass of 149. This composition is attractive because:

1) These compounds (identified on the basis of retention times and mass spectra) have been prepared from aqueous solutions from low molecular weight nitrogen-containing materials such as proline and pyrrolidine.
2) The bromine component of one (Peak #7) has been confirmed by decomposition using high intensity ultraviolet radiation and detection by a bromide-specific ion electrode.
3) A single nitrogen is indicated by the odd numbered molecular ion (assumed).

Identification of the source or parent reactants of these compounds in natural coastal water is severely hampered because specific compounds that have been distinguished by analysis account for less than 20% of the TOC present. The reaction and decomposition of several amino acids with halogen (primarily chlorine) have received attention as reviewed by Kovacic et al.[5] and Morris.[6] The halogenation of α-amino acids, such as alanine,[7] leads to products that decompose rapidly (deamination and decarboxylation), and these materials have been viewed primarily as "chlorine-consumers" that interfere with disinfection operations.

However, we have found that proline or hydroxyproline produces stable products that are observable as the fluorescent dansyl derivative in high-performance liquid chromatography. The first step appears to be decarboxylation with formation of 1-pyrroline,[8] which is in equilibrium with 4-amino-*n*-butyraldehyde. Further reaction with halogen by the 1-pyrroline results in compounds that include materials that correspond to the peak 7 and 9 compounds in

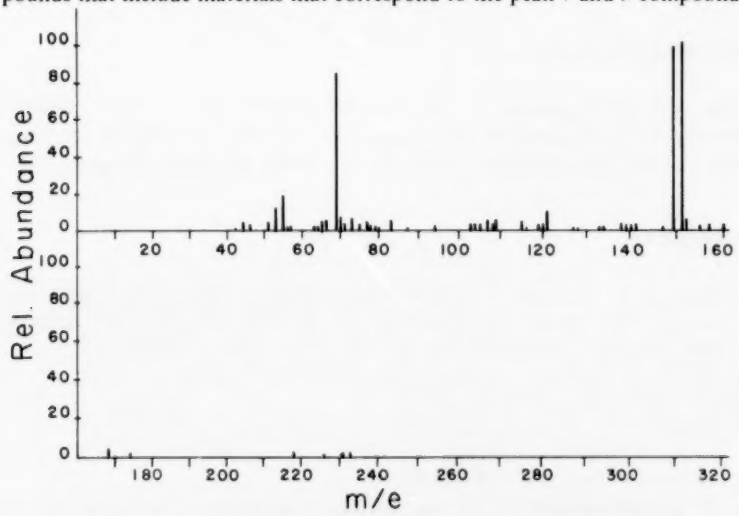

Figure 2. Mass spectrum of material eluting at 6.6 min (peak 7, Figure 1).

Figure 1. We have been able to synthesize these compounds by reacting proline with HOBr at 1:1 molar ratio, extraction of the product (presumably pyrroline) into ether, and addition of HOBr in ether to the extract with the formation of the peak 7 and 9 compounds, which supports the proposed reaction sequence.

Although proline is not a dominant constitutent of proteins, its high abundance in collagen (20-30%) makes it a potentially significant source of the lipophilic compounds that we have isolated. These compounds can also be synthesized in low yield from the reaction of pyrrolidine with HOBr. We have found that halogenation products of aqueous solutions of pyrrolidine are rather stable. Observation of the UV absorption at the halogen-nitrogen peaks shows a half-life of 68 hr for N-chloropyrrolidine and a half-life of 33 hr for N-bromopyrrolidine. Scully and Bempong[9] have reported that N-chloropiperidine is quite stable, and halogen-secondary amine compounds apparently deserve more study as possible environmental contaminants.

Although the identity of the substances responsible for the formation of the compounds represented in the Figure 1 chromatogram can only be conjectured, our observations show these reaction products may be quantitatively as important as the more extensively studied haloforms, with unknown environmental significance.

The next, crucial, step in this study is to isolate and identify these elusive compounds using laboratory synthesis followed by spectral and elemental analysis. This work is presently underway.

ACKNOWLEDGMENTS

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